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Tautomeric and Conformational Properties of Malonamide, $NH_2C(O){-}CH_2{-}C(O)NH_2$: Electron Diffraction and Quantum Chemical Study

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The geometric structure of malonamide, $NH_2C(O){-}CH_2{-}C(O)NH_2$, has been investigated by gas electron diffraction (GED) and quantum chemical calculations (B3LYP and MP2 approximations with 6-311++G(3df,pd) basis sets). Both GED and quantum chemistry result in the existence of a single diketo conformer in the gas phase. According to GED refinement this conformer possesses (sc,ac) conformation with one C=O bond in synclinal orientation (dihedral angle $\tau(O{=}C{-}C{-}C) = 49.0(3.0)°$) and the other C=O bond in anticlinal orientation (dihedral angle $\tau(O{=}C{-}C{-}C) = 139.5(3.3)°$). The experimental geometric parameters are reproduced very closely by the B3LYP method.

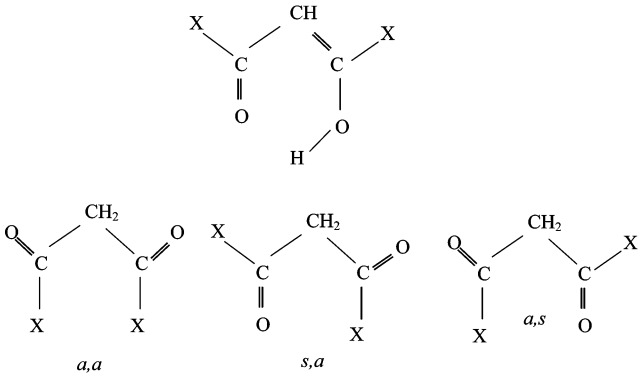
Introduction

The tautomeric properties of β-diketones (dicarbonyl compounds) of the type $XC(O){-}CH_2{-}C(O)Y$ have been a subject of continuous interest in chemistry.[1,2] The preference of an enol or keto tautomeric form depends strongly on the substituents X and Y. Structural studies in the gas phase show that the enol tautomer is preferred in compounds with X = Y = H,[3−5] CH_3,[6−8] $C(CH_3)_3$,[9] or CF_3[10] (group I). On the other hand, compounds with X = Y = F,[11] Cl,[12] or OCH_3[13] (group II) exist in the diketo form. Whereas a single conformer with a planar skeleton is expected for the enol form, three conformations are feasible for the diketo conformer (see Chart 1; "s" stands for synperiplanar (sp) or synclinal (sc) and "a" for antiperiplanar (ap) or anticlinal (ac)).[14]

In a previous investigation[15] we have studied the tautomeric and conformational properties of acetoacetamide, $CH_3C(O){-}CH_2{-}C(O)NH_2$ (AAM), a dicarbonyl compound which contains two different substituents X = CH_3 and Y = NH_2. In this case a gas electron diffraction (GED) study resulted in a mixture of 63(7)% enol and 37(7)% diketo tautomers. Quantum chemical calculations (MP2 and B3LYP with small and large basis sets) predict diketo contributions between 14% and 100%. Only the B3LYP method with small basis sets (6-31G(d,p)) reproduces the experimental data satisfactorily. From the experimental result we conclude that the presence of two substituents in AAM with different electronegativities leads to the existence of a mixture of keto and enol forms. Thus, X = CH_3 favors the enol tautomer, whereas Y = NH_2 favors the diketo form.

The present study deals with malonamide, $NH_2C(O){-}CH_2{-}C(O)NH_2$ (MA). Considering our results for AAM, where the NH_2 group was found to favor the diketo form, we expect the diketo tautomer to be strongly predominant in this dicarbonyl compound with both substituents X = Y being NH_2. The tautomeric and conformational properties of malonamide are important in understanding the chemistry of several classes of molecules including bioactive peptide analogues,[16−18] *n*,3 nylon polymers,[19,20] and metal ion sequestering agents.[21]

CHART 1: Enol Tautomer (above) and Three Possible Conformers of Diketo Tautomer of $XC(O){-}CH_2{-}C(O)Y$ Compounds with X = Y (below)



Several quantum chemical investigations of MA have been reported.[22−24] Two stable diketo conformations of malonamide, (sc,ac) and (ac,ap), have been predicted by different computational methods (HF, DFT, and MP2) with different basis sets.[23] These authors pointed out that the energy of the (ac,ap) conformer is higher than that of the (sc,ac) form by 4−6 kcal/mol. Schiavoni et al.[24] studied the conformational and tautomeric composition of malonamide by means of vibrational spectroscopy and by quantum chemical calculations. Solid-state Fourier transform infrared and Raman spectra were analyzed. They reveal the existence of a diketo tautomer. Theoretical calculations (HF/6-31G(d) and B3PW91/6-31G(d)) predict only one stable diketo structure belonging to the C_1 symmetry group. Two stable enol forms are predicted to have much higher energies than the diketo form.

No enol form is observed for solid MA. ^{13}C NMR studies of a solution of MA (D_2O was used for the field frequency stabilization and $(CH_3)_4Si$ as internal standard) show as well only signals of a diketo tautomer.[24] Similar results were obtained by Buemi et al.[22] with the B3LYP/6-31G(d,p) method. Calcula-

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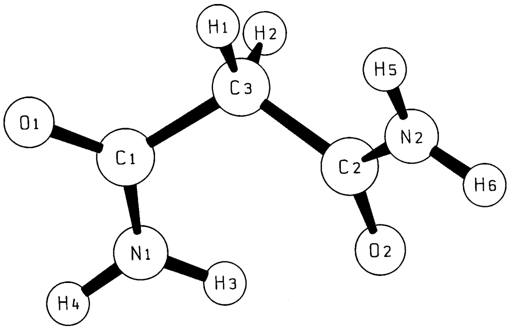

Figure 1. Molecular structure of malonamide.

tions with different fixed rotational angles around the C−C bonds demonstrate that an asymmetric diketo structure with dihedral angles of τ(O2C2C3C1) = 47.9° and τ(O1C1C3C2) = 140.1° (see Figure 1 for atom numbering) is the lowest in energy of all different conformations obtained by rotation around the C−C bond.

The crystals of MA are monoclinic with two molecules in the asymmetric unit.[25] Both symmetry-unrelated molecules possess different orientation in the crystal, but they have similar diketo conformations and dimensions. The amide groups are rotated out of the central C−C−C plane in both molecules, one by about τ(O1C1C3C2) = 65° and the other by about τ(O2C2C3C1) = 40°.

In the present study we report an investigation of the geometric structure and conformational properties of gaseous malonamide (MA), applying gas electron diffraction (GED) and quantum chemical calculations.

Results

Quantum Chemical Calculations. All quantum chemical calculations were performed with the program set Gaussian 03.[26] According to quantum chemical research by Schiavoni et al.,[24] two enol tautomers exist, but they are higher in energy by 13−18 kcal/mol than the diketo conformer. The absence of the enol form in solution of malonamide was demonstrated by NMR spectroscopy. Therefore, in the present study we performed quantum chemical calculations only for the diketo form.

To find all possible diketo conformers, the potential energy surface was scanned with the B3LYP/6-31G(d,p) method. The

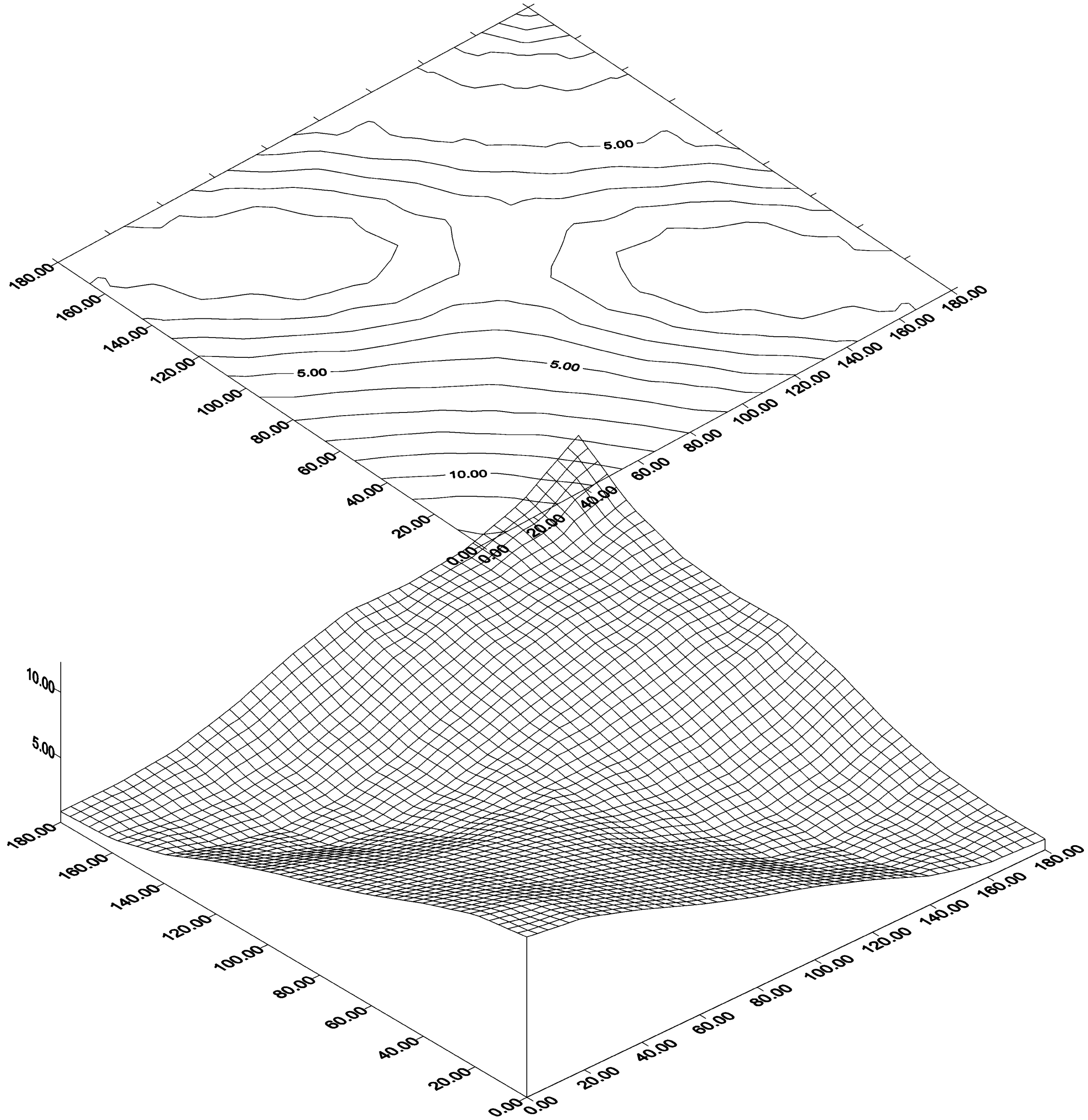

Figure 2. Potential energy surface for malonamide obtained by rotation around C−C bonds.

TABLE 1: Experimental and Calculated Geometric Parameters of Malonamide[a]

parameter	GED (r_{h1}, $\angle_{h1}$)[b]	B3LYP[c]	MP2[c]
r(C1−C3)	1.539(3)	1.536	1.528
r(C2−C3)	1.523(3)[d]	1.520	1.514
r(C1−O1)	1.218(3)	1.216	1.220
r(C2−O2)	1.224(3)[d]	1.222	1.225
r(C1−N1)	1.360(3)	1.351	1.354
r(C2−N2)	1.364(3)[d]	1.355	1.354
r(C3−H1)	1.088(4)	1.088	1.088
r(C3−H2)	1.095(4)[d]	1.095	1.093
r(N1−H3)	1.013(4)[d]	1.013	1.013
r(N1−H4)	1.007(4)[d]	1.007	1.008
r(N2−H5)	1.005(4)[d]	1.005	1.005
r(N2−H6)	1.008(4)[d]	1.008	1.009
∠C1C3C2	114.7(1.0)	116.0	113.2
∠C3C1O1	119.5(0.5)	120.1	121.1
∠C3C2O2	122.0(0.5)[d]	122.6	122.1
∠N1C1C3	115.5(0.8)	115.6	114.6
∠N2C2C3	115.4(0.8)[d]	115.5	115.5
∠H1C3C1	106.7[e]	106.7	107.1
∠H1C3C2	112.6[e]	112.6	113.0
∠H2C3C1	106.9[e]	106.9	107.7
∠H2C3C2	106.5[e]	106.5	106.9
∠H3N1C1	119.4[e]	119.4	119.0
∠H4N1C1	118.0[e]	118.0	117.6
∠H5N2C2	122.3[e]	122.3	121.9
∠H6N2C2	118.6[e]	118.6	118.5
τ(O1C1C3C2)	139.5(3.3)	142.9	135.0
τ(O2C2C3C1)	49.0(3.0)	49.8	60.5
τ(N1C1C3O1)	176.8(2.2)	177.1	177.2
τ(N2C2C3O2)	178.6(2.2)[d]	178.9	179.9
τ(H3N1C1C3)	12.3[e]	12.3	14.7
τ(H4N1C1O1)	−6.1[e]	−6.1	−7.9
τ(H5N2C2C3)	3.5[e]	3.5	3.7
τ(H6N2C2O2)	−0.4[e]	−0.4	−1.8

[a] Distances in angstoms and angles in degrees. For atom numbering see Figure 1. [b] Uncertainties for bond lengths $\sigma = (\sigma_{sc}^2 + (2.5\sigma_{LS})^2)^{1/2}$ ($\sigma_{sc} = 0.002r$; σ_{LS}, standard deviation in least-squares refinement), for angles $\sigma = 3\sigma_{LS}$. [c] 6-311++G(3df,pd) basis sets. [d] Difference from previous parameter fixed to calculated (B3LYP) value. [e] Not refined.

torsional angles τ(O1C1C3C2) and τ(O2C2C3C1) were changed in steps of 20° with full optimization of all other parameters. Two deep and energetically equivalent minima on the potential energy surface were obtained for torsional angles of 40° and 140° ((sc,ac) or (ac,sc) conformer, respectively). Figure 2 shows the potential energy surface obtained by rotation around both C−C bonds.

The geometry of this diketo conformer of malonamide was fully optimized with the MP2 and B3LYP methods and 6-311++G(3df,pd) basis sets. The geometric parameters derived with both methods are summarized in Table 1, together with the experimental results. It should be noted that all geometric parameters optimized at different levels of theory are very close, except for the torsional angles τ(OCCC).

Vibrational amplitudes (l) and corrections, $\Delta r = r_{h1} - r_a$, were derived from a theoretical force field (B3LYP/6-311++G(3df,pd)) with the method of Sipachev, using the program SHRINK.[27] The values of l and Δr are included in Table 2.

Structural Analysis. The experimental geometric structure of MA was determined with a combined GED/mass spectrometric method. The heaviest ion in the mass spectrum corresponds to the parent ion $[C_3H_6N_2O_2]^+$ (see the Experimental Section). This demonstrates that monomers are present in the vapor at the conditions of the GED experiment. No ions were detected, which could arise from impurities. The experimental radial distribution function (Figure 3) was derived by Fourier transformation of the experimental intensities. Comparison with calculated radial distribution functions demonstrates that the experimental curve can be reproduced very well with a single diketo tautomer (see Figure 3).

Differences between all C−H and N−H bond lengths, between C1−O1 and C2−O2 bond lengths, between C1−C3 and C2−C3 bond lengths, between ∠C3C1O1 and ∠C3C2O2 angles, between ∠N1C1C3 and ∠N2C2C3 angles, and between τ(N1C1C3O1) and τ(N2C2C3O2) torsional angles, as well as all angles which determine the position of H atoms, were constrained to calculated values (B3LYP/6-311++G(3df,pd)). The geometric parameters of MA using B3LYP/6-311++G(3df,pd) results as starting parameters

TABLE 2: Interatomic Distances r_{h1}, Vibrational Amplitudes l, and Vibrational Corrections $r_{h1} - r_a$ for Malonamide (Excluding Nonbonded Distances Involving Hydrogen)[a]

	r_{h1},[b] Å	l(GED)[b]	l(B3LYP)[c]	$r_{h1} - r_a$[c]
N2−H5	1.005(4)	0.070(2) $l1$[d]	0.070	0.0023
N1−H4	1.007(4)	0.069(2) $l1$	0.069	0.0047
N2−H6	1.008(4)	0.070(2) $l1$	0.070	0.0023
N1−H3	1.013(4)	0.070(2) $l1$	0.070	0.0060
C3−H1	1.088(4)	0.076(2) $l1$	0.076	0.0008
C3−H2	1.095(4)	0.077(2) $l1$	0.077	0.0014
C1−O1	1.218(3)	0.038(2) $l1$	0.038	−0.0008
C2−O2	1.224(3)	0.038(2) $l1$	0.038	0.0004
C1−N1	1.360(3)	0.045(2) $l1$	0.045	0.0131
C2−N2	1.364(3)	0.044(2) $l1$	0.044	−0.0003
C3−C2	1.523(3)	0.053(2) $l1$	0.053	0.0026
C3−C1	1.539(3)	0.054(2) $l1$	0.054	−0.0014
O2···N2	2.271(5)	0.051(4) $l2$	0.055	0.0049
O1···N1	2.287(5)	0.051(4) $l2$	0.054	0.0141
C3···O1	2.388(6)	0.062(4) $l2$	0.065	0.0071
C3···O2	2.407(6)	0.061(4) $l2$	0.064	0.0037
C3···N2	2.443(7)	0.063(4) $l2$	0.066	0.0036
C3···N1	2.453(7)	0.063(4) $l2$	0.067	0.0027
C2···C1	2.579(14)	0.085(4) $l2$	0.089	−0.0145
O2···N1	2.776(16)	0.187(11) $l3$	0.164	−0.0649
C2···N1	2.931(16)	0.140(11) $l3$	0.117	0.0499
C1···O2	3.009(12)	0.135(11) $l3$	0.112	−0.0708
C2···O1	3.603(13)	0.136(12) $l4$	0.140	−0.0431
C1···N2	3.657(24)	0.190(12) $l4$	0.194	0.0530
N1···N2	4.207(35)	0.206(10) $l5$	0.206	0.1726
O1···O2	4.177(15)	0.120(13) $l6$	0.134	−0.0853
O1···N2	4.467(44)	0.292(13) $l6$	0.306	0.0050

[a] Values in angstroms. Error limits are 3σ values. For atom numbering see Figure 1. [b] r_{h1}, l(GED): interatomic distances and vibrational amplitudes derived from GED data. [c] Derived from theoretical force field (B3LYP/6-311++G(3df,pd)) with the method of Sipachev, using the program SHRINK.[27] [d] Group number of amplitude.

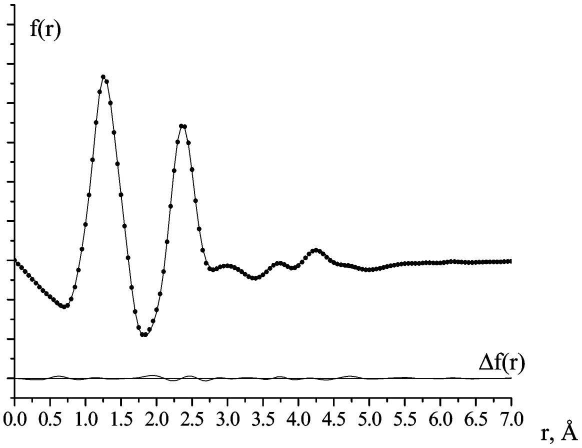

Figure 3. Experimental (dots) and theoretical (solid lines) radial distribution curves and the difference (experimental − theoretical).

TABLE 3: Geometric Parameters of Crystal and Gas-Phase Molecules of Malonamide[a]

	X-ray data[25]	GED, r_{h1}
r(C−C)	1.507^b (8)[c]	1.539 (3)
		1.523 (3)
r(C−N)	1.334^b (7)	1.360 (3)
		1.364 (3)
r(C=O)	1.253^b (7)	1.218 (3)
		1.224 (3)
∠C−C−N	117.6^b	115.5 (0.8)
		115.4 (0.8)
∠C−C=O	119.9^b	119.5 (0.5)
		122.0 (0.5)
∠N−C=O	122.6^b	124.9 (1.0)
		122.5 (1.0)
τ(N−C−C−C)	40	43.6 (2.5)
	65	132.4 (2.5)

[a] Distances in angstroms and angles in degrees. [b] Average value. (C−C and C−N distances are corrected for thermal libration.[25]) [c] Values in parentheses represent standard deviations for X-ray data and full uncertainties for GED (see notes for Table 1).

TABLE 4: Conditions of GED Experiment

nozzle-to-plate distance, mm	338.0	598.0
fast electron beam, μA	1.5	0.7
accelerating voltage, kV	73.7	74.4
electron wavelength, Å	0.043648(60)	0.043437(30)
temperature of effusion cell, K	435(3)	434(3)
ionization voltage, V	50	50
exposure time, s	70−75	60−70
residual gas pressure, Torr	2×10^{-6}	3×10^{-6}

were then refined by a least-squares procedure of the molecular intensities. Independent r_{h1} parameters were used to describe the molecular structure. Vibrational amplitudes were collected in six groups, and differences within each group were fixed to calculated values. With these assumptions nine geometric parameters and six vibrational amplitudes were refined simultaneously. There were only three correlation coefficients that had values larger than |0.7|: ∠C2C3C1/τ(O2C2C3C1) = −0.84, ∠N1C1C3/∠O1C1C3 = −0.82, and τ(O1C1C3C2)/τ(N1C1C3O1) = −0.88. The agreement factor for a single diketo conformer in the vapor at 161(4) °C was R_f = 4.9%. Final results of the least-squares analysis are given in Table 1 (geometric parameters) and Table 2 (vibrational amplitudes; the refined groups are designated as l1, l2, etc.).

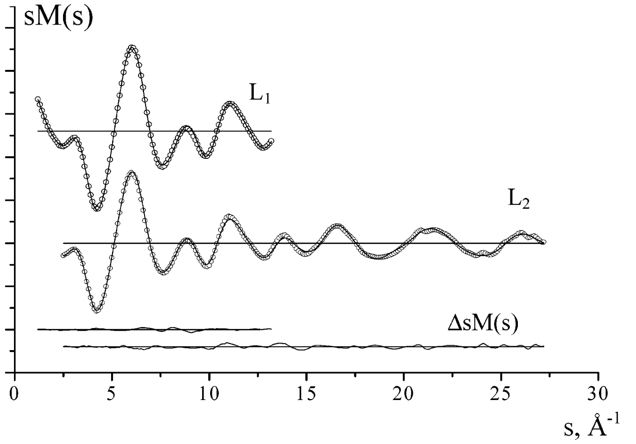

Figure 4. Experimental (dots) and calculated (solid lines) modified molecular intensity curves and the residuals (experimental − theoretical) at two nozzle-to-plate distances (L_1 = 598 mm, L_2 = 338 mm).

TABLE 5: Mass Spectral Data of the Vapor of $C_3H_6N_2O_2$

ion	m/e	abundance, %
$[M]^{+a}$	102	11
$[M - 2NH_2 - 2H]^+$	68	4
$[NH_2C(O)CH_3]^+$	59	100
$[C(O)NH_2]^+$	44	68
$[C(O)NH]^+$	43	42
$[C(O)CH_2]^+$	42	43

[a] M = $C_3H_6N_2O_2$.

Discussion

The GED experiment for malonamide, $NH_2C(O)-CH_2-C(O)NH_2$, which is a dicarbonyl compound with two NH_2 groups as substituents, results in the presence of a single diketo conformer in the gas phase at 161(4) °C. This result is in agreement with the predictions by quantum chemical calculations which were performed in this study and in a previous study by Schiavoni et al.[24] It is in contrast to predictions reported by Sandrone et al., who reports the existence of two stable keto forms.[23] The experimental geometric parameters are reproduced closely by the B3LYP/6-311++G(3df,pd) method.

As pointed out in the Introduction, the tautomeric properties of dicarbonyl compounds XC(O)−CH_2−C(O)Y depend strongly on the substituents X and Y. In malonamide both substituents, X = Y = NH_2, possess a group electronegativity of χ_{BB} = 3.12.[28] According to the rule formulated by us previously,[15] substituents with $\chi_{BB} \geq 3.0$ favor the diketo form. An alternative characterization of the substituents which determine the keto−enol tautomeric properties is the absence or presence of electron lone pairs, whereby substituents without lone pairs, such as H, CH_3, $C(CH_3)_3$ or CF_3 favor the enol form and substituents with lone pairs, such as F, Cl, and OCH_3, favor the diketo form.[15] NH_2 groups possess one lone pair and thus favor the diketo form. Both rules formulated above are crude and mainly intuitive. However, in the case of malonamide both, the electronegativity of substituents and the presence of electron lone pairs, predict the existence of MA as a diketo tautomer only.

The structural parameters of malonamide refined from GED may be compared with the X-ray data[25] (Table 3). The main difference between GED and crystal structures is the orientation of the keto groups. GED results in an (sc,ac) conformer, but crystal data correspond to an (sc,sc) form. The (sc,ac) conformation present in the gas phase is stabilized by a weak intramolecular N−H···O hydrogen bond (r(O2···H3) = 2.021(24) Å). Intermolecular hydrogen bonds and packing effects, however, seem to favor the (sc,sc) orientation of the two keto groups in the crystal.

Several effects may contribute to differences between bond distances determined by X-ray crystallography and by gas electron diffraction: (1) intermolecular interactions in the crystal, such as hydrogen bonding, (2) a shift of the maximum of the electron density relative to the position of the nucleus of the respective atom, (3) vibrational effects, including lattice vibrations in the crystal, and (4) possible different conformational properties in the crystal and in the gas phase. It is very difficult to estimate quantitative values for these individual contributions. Taking into account these various effects, the differences in $\mathrm{C{-}C}$ and $\mathrm{C{-}N}$ bond lengths, which are shorter in the crystal than in the gas phase, and in the $\mathrm{C{=}O}$ length, which is longer, are not surprising.

Experimental Section

A commercial sample (Merck, $>98\%$) was used. The electron diffraction patterns and the mass spectra were recorded simultaneously using the techniques described previously.[29,30] The conditions of the GED/MS experiment and the relative abundance of the characteristic ions of $C_3H_6N_2O_2$ are shown in Tables 4 and 5, respectively. The temperature of the stainless steel effusion cell was measured by a W/Re-5/20 thermocouple that was calibrated by the melting points of Sn and Al. The wavelength of electrons was determined from diffraction patterns of polycrystalline ZnO. The optical densities were measured by a computer controlled MD-100 microdensitometer.[31] The molecular intensities $sM(s)$ were obtained in the s-ranges $2.5-27.2$ and $1.2-13.2$ Å^{-1} for the short and long nozzle-to-plate distances, respectively ($s = (4\pi/\lambda)\sin(\theta/2)$; λ is electron wavelength and θ is scattering angle). The experimental and theoretical intensities $sM(s)$ are compared in Figure 4.

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Supporting Information Available: Atomic coordinates for the (sc,ac) diketo conformer of malonamide. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) "sp" corresponds to dihedral angle $\tau(\mathrm{C{-}C{-}C{=}O}) = 0 \pm 30°$, "sc" to $\tau = 60 \pm 30°$, "ac" to $\tau = 120 \pm 30°$, and "ap" to $\tau = 180 \pm 30°$.

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